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13. ABSTRACT (Maximum 200 words)

We have extensively studied, both experimentally and theoretically, the following three mixed-halide systems:
(1) $\text{PtCl}_x\text{Br}_{1-x}$, (2) $\text{PtCl}_x\text{I}_{1-x}$ and (3) $\text{PtBr}_x\text{I}_{1-x}$ for a variety of concentrations x . We have obtained direct spectroscopic
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polarons are trapped within PtCl segments. This polaron charge selectivity, which is potentially very useful for photovol-
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binding, extended Peierls-Hubbard model, showing strong hybridization of PtCl and PtBr electronic bands as the driving
force for separation. In contrast to $\text{PtCl}_x\text{Br}_{1-x}$, we find that both the $\text{PtCl}_x\text{I}_{1-x}$ and the $\text{PtCl}_x\text{Br}_{1-x}$ systems exhibit
qualitatively different behavior, such as intrinsic "self doping." In other words, our simulations predict that electronic
charge is spontaneously removed from the PtI segment and injected into the PtCl (or PtBr) segment, thus creating hole
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PHOTOINDUCED ELECTRON-HOLE CHARGE SEPARATION, INTRINSIC
SELF-DOPING AND NOVEL DEVICE APPLICATIONS OF Q1D HETERO-
JUNCTION MATERIALS: MIXED-HALIDE MX SOLIDS

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We have extensively studied, both experimentally and theoretically, the following three mixed-halide systems: (1) $\text{PtCl}_x\text{Br}_{1-x}$, (2) $\text{PtCl}_x\text{I}_{1-x}$ and (3) $\text{PtBr}_x\text{I}_{1-x}$ for a variety of concentrations x . We have obtained direct spectroscopic evidence (vibrational modes) for charge separation from resonance raman (RR) experiments on doped and photoexcited single crystals of $\text{PtCl}_x\text{Br}_{1-x}$. In particular, electron polarons preferentially locate on the PtBr segment while hole polarons are trapped within PtCl segments. This polaron charge selectivity, which is potentially very useful for photovoltaic device applications, is demonstrated within theoretical calculations based on a discrete, 3/4-filled, two-band, tight-binding, extended Peierls-Hubbard model, showing strong hybridization of PtCl and PtBr electronic bands as the driving force for separation. In contrast to $\text{PtCl}_x\text{Br}_{1-x}$, we find that both the $\text{PtCl}_x\text{I}_{1-x}$ and the $\text{PtBr}_x\text{I}_{1-x}$ systems exhibit qualitatively different behavior, such as intrinsic "self doping". In other words, our simulations predict that electronic charge is spontaneously removed from the PtI segment and injected into the PtCl (or PtBr) segment, thus creating hole defects in PtI and electron defects (polarons/bipolarons) in PtCl (or PtBr).

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I. INTRODUCTION

Halogen-bridged transition metal complexes (or MX chains), as well as being important in their own right, provide an important test case for theoretical techniques

and issues in low-dimensional materials with strong electron-electron and electron-phonon interactions [1-3]. This is particularly true because of the extreme range of broken-symmetry ground states that are achieved by varying M (Pt, Pd, Ni) and X (Cl, Br, I, etc.) as well as ligands, pressure, magnetic field—ground states ranging from a strongly disproportional CDW (e.g. PtCl) to a weak CDW (e.g. PtI) to SDW or spin-Peierls (and other mixed CDW/SDW [4]) phases (e.g. NiBr, NiCl), in addition to long-period “superlattice” structures [5]. Here we focus on the important consequences of mixing two CDW materials ($\text{PtX}_x\text{X}'_{1-x}$) with differing strength of CDW amplitudes. We have modeled effective isolated single chains of MX materials in terms of a 3/4-filled, 2-band Peierls extended-Hubbard model. In an isolated mixed-halide chain [6] we replace a segment, containing m X atoms, by m X' atoms where $\text{X}, \text{X}' = \text{Cl}, \text{Br}, \text{I}$.

II. PHOTOINDUCED CHARGE SEPARATION

In this section we briefly describe photoinduced charge separation in $\text{PtCl}_x\text{Br}_{1-x}$ both as observed in resonance Raman (RR) experiments and simulations within the Peierls-Hubbard model.

In the RR experiment, upon photolysis of mixed-halide materials, photoinduced charged defects were produced in high concentration. Fig. 1 depicts the RR spectrum probed at 1.34 eV of a mixed $\text{PtCl}_{.75}\text{Br}_{.25}$ crystal before and after photolysis at 2.54 eV (beyond the band edge of pure PtCl). This is an excitation energy (1.34 eV) where resonance enhancement is known to occur for the P^+ and P^- in PtCl, and a region of pre-resonance for the electron bipolaron and P^- in PtBr. Prior to photolysis the $\text{Cl}-\text{Pt}^{IV}-\text{Cl}$ symmetric stretch chain mode at 308 cm^{-1} dominates the spectra

Weak features at ~ 285 and 325 cm^{-1} are attributed to P^- defects and edge state modes in PtCl segments, respectively. In the spectral region for PtBr, modes at 213 and 181 cm^{-1} are observed which are vibrational signatures for PtBr edge states. The broad feature at 150 cm^{-1} is ascribed to a P^- in a PtBr segment. Photolysis within the band gap of PtCl and in the ultragap region of PtBr (2.54 eV) causes an increase in P^+ defects localized within the PtCl segments at $\sim 285\text{ cm}^{-1}$. These results are in contrast to the photolysis of pure materials: in pure crystals of PtCl, RR studies show an increase in *both* P^- (263 cm^{-1}) and P^+ (287 cm^{-1}) local modes. Significantly, in the mixed materials, *no* P^- features appear in the PtCl segments with photolysis. In the PtBr segments, the P^- defect at 150 cm^{-1} also increases in intensity. In a second experiment, photolysis on a mixed crystal of $\text{PtCl}_{.95}\text{Br}_{.05}$ exhibited similar results [6].

To illustrate charge separation within our model we systematically studied the lattice relaxation. Upon doping, if we initially placed a P^- in the PtCl segment (*i.e.*, the “wrong” segment) and allowed the system to self-consistently evolve to the minimum energy configuration, we found the P^- migrated to a Pt^{IV} site in the PtBr segment (Fig. 2). A P^+ placed in the PtBr segment similarly migrated to a Pt^{II} site in the PtCl segment. Analogously, the photogenerated exciton was invariably unstable and broke into a P^+ and a P^- , the P^+ migrating to the PtCl segment and its companion P^- to the PtBr segment. Both doping and photoexcitation lead to charge separation with a specific polaron charge selectivity consistent with experimental observations. The analysis of electronic wavefunctions revealed strong hybridization of PtCl and PtBr electronic bands as the driving force for charge separation.

III. INTRINSIC SELF-DOPING

Apart from the $\text{PtCl}_x\text{Br}_{1-x}$ mixed-halide system discussed above we also explored $\text{PtCl}_x\text{I}_{1-x}$ and $\text{PtBr}_x\text{I}_{1-x}$ systems. Quite interestingly, these systems exhibit qualitatively different behavior such as intrinsic "self doping". In other words, based on the above experimental and theoretical techniques we find that electronic charge is spontaneously removed from the PtI segment and injected into the PtCl (or PtBr) segment, thus creating hole defects in PtI and electron defects (polarons/bipolarons) in PtCl (or PtBr).

Experimentally we studied resonance Raman (RR) spectra both as a function of PtI concentration and excitation energy. The fundamental symmetric stretch (ν_1) modes for PtI (113 cm^{-1}) and for the other constituent, PtCl (or PtBr), develop fine structure. In addition, a few other lines are seen in the RR spectra [7]. The number of lines in the fine structure varies with the concentration x of PtCl (or PtBr) and each one of these lines comes into resonance at a different excitation energy. We are in the process of assigning specific vibrational modes to these lines based on the above theoretical model. Further, X-ray diffraction experiments in conjunction with thermal ellipsometric studies reveal that, subsequent to the formation of a mixed-halide crystal, the PtI segment contracts while the PtCl (or PtBr) segment expands [8].

Fig. 3 depicts excess charge density with respect to the corresponding charge-density-wave (CDW) ground state in each segment as predicted by the two-band Peierls-Hubbard model for $\text{PtCl}_x\text{I}_{1-x}$ (Fig. 3a) and $\text{PtBr}_x\text{I}_{1-x}$ (Fig. 3b). Clearly, one observes formation of electron bipolarons in the PtCl (or PtBr) segment (as well as at the interface) with a concomitant formation of hole bipolarons in the PtI segment.

However, since PtI is a very delocalized system (the correlation length of a bipolaron is very long) the hole bipolarons are squeezed into a small segment of PtI. Therefore, the shape of a bipolaron in a PtI segment is not as clearly visible as in the PtCl (or PtBr) segment. The driving force for the ejection of electrons from PtI into PtCl (or PtBr) can be understood from the calculated electronic band structure (not shown here). The highest unoccupied PtCl (or PtBr) electronic state is found to be lower in energy than the lowest occupied Pt-band of PtI. The system lowers its electronic energy by pumping electrons into the PtCl (or PtBr) bands from the PtI (self-doping). From this perspective the PtI based mixed-halide systems behave like an intrinsic p-n junction. Further analysis of theoretical results shows that the PtI segment contracts while PtCl (or PtBr) expands consistent with the x-ray diffraction experiments [8]. We are in the process of exploring dielectric, IR, RR, ESR, DC/AC conductivity, nonlinear optical (NLO) and other interesting properties to further characterize these novel electronic materials.

IV. DEVICE APPLICATIONS AND CONCLUSIONS

Above discussion suggests the possibility of fabricating Q1D devices that utilize polaronic charge separation/injection. We emphasize that, from a band structure point of view, mixed-halide chains represent a 1D analog of heterojunctions in semiconductors. When light is shone on such a device the photogenerated electrons migrate to the PtBr side of the junction while the holes move to the PtCl side. Thus, an open circuit voltage develops across the device and essentially one has a mixed-halide MX crystal based solar cell. Similarly, as indicated above, $\text{PtX}_x\text{I}_{1-x}$ chain materials are one-dimensional analogs of p-n junctions. We are also in the process of modeling

a compositional superlattice based on PtCl/PtBr system.

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FIGURE CAPTIONS:

Fig.1 Resonance Raman (RR) spectra at 1.34 eV of $\text{PtCl}_{0.75}\text{Br}_{0.25}$ mixed-halide crystal (a) before and (b) after photolysis with 2.54 eV excitation at 2 mW for 1.5 hours at 13 K. (c) Difference spectra: Post-photolysis intensity minus pre-photolysis intensity.

Fig.2 Excess charge (—) and spin (---) densities with respect to the mixed-chain ground state showing polaron migration for (a) P_1^- and (b) P_1^+ on a 16 PtCl and 8 PtBr unit chain, and (c) subsequent to photoexcitation of an up spin electron between levels 36 and 37 on an 8 PtCl and 16 PtBr unit chain. The large circles indicate initial defect location, though the result is insensitive to initial condition.

Fig.3 Excess charge density with respect to the corresponding CDW ground state in each segment for (a) $\text{PtCl}_x\text{I}_{1-x}$, and (b) $\text{PtBr}_x\text{I}_{1-x}$.





